Summary of Doctoral Dissertation (Doctoral Program (Science))

by
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Title: Synthetic Studies on Pyrene-Based π-Expanded Ligands and Their Transition Metal Complexes
ピレンを用いたπ電子拡張型金属錯体の合成研究（英文）"English"

Summary

Salicylaldimine is one type of the Schiff base ligands to form chelate using N and O atoms and known to produce complexes with most of the transition metals such as Pt^{2+}, Pd^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, etc. So far, many salicylaldimine-type ligands and their complexes have been reported. Because the benzene moiety of salicylaldimine has excellent designability, many chemical modifications were carried out using electrophilic substation reactions. Replacement of the benzene nucleus to other aromatic molecule such as naphthalene is also widely used strategy because the expanded π-electronic system delocalizes the *d*-orbitals of the metal. Therefore, the enhanced properties were reported for this class of complexes.

Pyrene is one of the popular π-expanded aromatic hydrocarbons. Because this molecule shows a strong emission with a long lifetime and high quantum yield, concentrate and solvent dependent excimer formation, high conductivity of their cation radical salt, pyrene is one of the key material for the contemporary interdisciplinary science.

This thesis describes a molecular design and syntheses of pyrene-based salicylaldimine-type ligands and the corresponding metal complexes. Other than the specific properties described before, molecular orbital character motivate the author applying pyrene as a component nucleus of the ligands.

Several studies on pyrene-based complexes have been documented in which the pyrene behaves as a pendant to a common ligand or organometallic pyrene complexes. The salicylaldimine-type ligands of pyrene have already been utilized to prepare for sensors and organic light-emitting diodes. However, as far as we know, there exists no report on salicylaldiminato-type transition-metal complexes of pyrene. Moreover, salicylaldiminato-based metal complexes are currently still an interesting research objects for catalysts, sensors and organic devices; a new research orientation will be opened to find metal complexes of rich π-electron ligands for the applications. This thesis demonstrates that the expansion of the π electronic system of ligand, the position changes of functional groups and the introduction of the bulkyl group on position-7 of pyrene and on imine group can generate significant changes in the electronic, photophysical, and structural properties of the salicylaldiminato-type transition metal complexes. This thesis consists of seven chapters including general introduction (Chapter 1) and general experimental (chapter 2).

Chapter 3. Syntheses and Characterizations of 1-hydroxy-2-[(alkylimino)methyl]-pyrene (1) and the Corresponding Metal Complexes (1(M))

In order to open my chemistry, a pyrene-based salicylaldimine-type ligand, 1-hydroxy-2-[(octylimino)methyl]-pyrene **1**, were designed and synthesized from commercially available pyrene in six steps.[1,4] Several metal complexes would be my target focusing on the properties intrinsic to each metal. For example, Pt complex has a potential for light emitting materials, Pd(II) for a catalysis, Co for an oxygen transport material.

Currently, the following metal complexes are prepared and characterized: Co(II), Co(III), Cu(II), Ni(II), Pd(II), and Pt(II). Among these metal complexes, group-ten elements, Ni(II), Pd(II), and Pt(II), and Cu(II) complexes take four coordination structures and show narrow HOMO-LUMO gap that are confirmed by absorption spectra, red shifts, and electrochemical studies, lower oxidation potentials, compared with those of the corresponding salicylaldiminato complexes. Especially, nickel and copper complexes display polymorphism phenomena that have been focused and developed recently for energy storage materials.

Furthermore, complex formation reactions with cobalt (II) salt show interesting behaviors. The reaction of **1** (R = $^{n}C_8H_{17}$) with Co(II) acetate induced oxidation reaction of the metal and afforded Co(III)$\mathbf{1}_3$. When the alkyl substituent of imine was replaced by bulky one, the Co(II)$\mathbf{1}_2$ was obtained. Therefore, the bulkiness of the alkyl group on imine controls the oxidation of Co. The obtained Co(II) and Co(III) complexes were characterized to be tetrahedral four coordinate and octahedral six coordinate meridional complexes, respectively.

Chapter 4. Syntheses and Charaterizations of 2-hydroxy-1-[(alkylimino)methyl]-pyrene (2) and the Corresponding Metal Complexes (2(M))

The characteristics of the molecular orbital of pyrene should be that 2- and 7-positions are node of both HOMO and LUMO. The ligand described in the previous chapter has hydroxyl group at 1-position and imine at 2-position. Therefore, an isomer **2** having hydroxyl group at 2-position and imine at 1-position would induce different properties because the former ligand 1 is mainly affected electron donating hydroxyl group, contrary, isomeric **2** mainly involves electron withdrawing imine group. The molecular design, syntheses, and characterizations of new ligand (**2**) and the corresponding metal complex (**2(Pt)**) were carried out.[2] The keys of this synthesis were 1) introduction of hydroxyl group at 2-position and 2) ortho-lithiation and the subsequent formulation. Although **2(Pt)** takes similar to that of **1(Pt)**, the *trans*-configuration of the ligands and square planar coordination geometry, the Pt-O coordination bond distances are different, *i.e.*, 1.953 and 1.991 Å for **2(Pt)** and **1(Pt)**, respectively. In addition, the shapes of the absorption spectra of the complexes are also different. The most interesting point is that the phosphorescence lifetime of the isomeric platinum complex **2(Pt)** is longer than that of the complex **1(Pt)**. In this part, the syntheses and characterizations of **2** and **2(Pt)** will be discussed with special emphasis on the relationship between properties and their molecular orbitals.

Chapter 5. Syntheses and Characterizations of New Pyrene-Based Salicylaldiminato Ligands and Corresponding Zinc(II) Complexes

Recently, luminescent materials have attracted much attention due to their significant expansibility in commercial applications such as OLEDs. Among of them, bis(salicylaldiminato) zinc complexes were reported to be effective emitters having good electron transport capability in a two-layer cell structure. In order to enhance the luminescent properties of these complexes, modification of the corresponding ligands is needed. Therefore, a series of pyrene-based salicylaldimine-type ligands containing n-octyl or cyclohexyl or phenyl groups at imine nitrogen group, 1-hydroxy-2-[(N-substituted-imino)methyl]-pyrenes (octyl **1**, cyclohexyl **1b** and phenyl **1c**) were synthesized and characterized. The reaction of ligands with zinc acetate in the presence of sodium acetate gave the bis(salicylaldiminato)-type Zn(II) complexes [bis[2-[(N-substituted-imino)methyl]-1-pyrenolato-N,O] zinc(II)] (octyl **1(Zn)**, cyclohexyl **1b(Zn)**, phenyl **1c(Zn)**). The new ligands and complexes were characterized by ^{1}H NMR, IR spectroscopy, mass spectroscopy, elemental analysis, UV-vis spectroscopy, fluorescence spectroscopy, and X-ray diffraction. The influence of the π-extended conjugation of the pyrene-based salicylaldiminato-type ligands coordinated to Zn^{2+} greatly induces red-shift of the complexes **1(Zn), 1b(Zn)** and **1c(Zn)** in absorption spectra.

While the emission of the complexes **1(Zn)** and **1b(Zn)** shows emission in green spectral region (λ_{max} = about 543 nm), the complex **1c(Zn)** shows emission in red spectral region (λ_{max} = 622 nm), indicating extension of the delocalized π-orbitals to the phenyl group on imino group. Single crystal structure of simple salicylaldiminato Zn(II) complex **1'b(Zn)** was compared to that the corresponding pyrene-type salicylaldiminato complex **1b(Zn)**. They have different coordination geometries, **1b(Zn)** takes tetrahedral coordination geometry while **1'b(Zn)** takes stair-stepped geometry; the Zn-O coordination bond distances are different, *i.e.*, 1.946 (1.928) and 1.891 Å for **1b(Zn)** and **1'b(Zn)**, respectively. These results were confirmed by density-functional theory (DFT) and time-dependent DFT (TDDFT) orbital calculations.

Chapter 6. Syntheses and Characterizations of Platinum Complexes with New Pyrene-based Salicylaldiminato-type Ligands that Subtituted at Position-7 of Pyrene

Many experimental data show that bulky substituents on the molecules enhance solubility, catalytic activity and photophysical properties due to the prevention of π-π stacking in metal salicylaldimines. In order to understand the effect of bulkiness of substituents on the properties of the obtained molecules, we researched and synthesized two new pyrene-based salicylaldiminato-type ligands that were substituted at position-7 and functionalized on imine group with bulkyl substituents. After introducing the tert-butyl group at position-7 of pyrene by Friedel-Crafts reaction, the syntheses of new ligands 1-hydroxy-2-[((2,6-dimethylphenyl)-imino)methyl]-7-(tert-butyl)-pyrene **3**, 2-hydroxy-1- [((2,6-dimethylphenyl)imino)methyl]-7-(tert-butyl)-pyrene **4** and corresponding platinum complexes **3(Pt)**, **4(Pt)** were performed in the similar way with the synthetic processes of the complexes **1(Pt)** and **2(Pt)**. The new ligands and complexes were characterized by ^{1}H NMR, IR spectroscopy, mass spectroscopy, elemental analysis and X-ray diffraction, only for **3(Pt)**. In addition to measurements of the absorption and emission spectra, TDDFT calculations using the B3LYP functionals were also performed. The complexes **3(Pt)** and **4(Pt)** exhibit good solubility and red-shift in absorption and emission spectra because of tert-butyl group at position-7 of pyrene and extension of the delocalized π-orbitals to the 2,6-dimethylphenyl on imine group.

Chapter 7. Conclusions.

As outlined in the results section, pyrene as the main π-skeleton can be used to synthesize a wide range of new salicylaldiminato-type transition metal complexes in high yielded six-step synthesis. In addition, the optical absorption and fluorescence properties can be easily shifted by replacing metal in the complexes and changing the coordinating positions of the ligands. Furthermore, the bulkiness of the alkyl group on imine of the ligands controls the oxidation state of cobalt. For cobalt(III) complex, the selective product, the meridional isomer, was obtained due to the steric repulsion of the ligands. Polymorphism phenomenon of copper and nickel complexes creates the great potential in the development of energy storage materials. Currently, these complexes are expected to apply for catalysts of coupling reactions and polymerizations as well as organic devices. Besides, we have been improving not only the structural, electrochemical and photophysical properties but also catalytic activity of the complexes by functionalizing on the ligands. These works are in research and development.

References.

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